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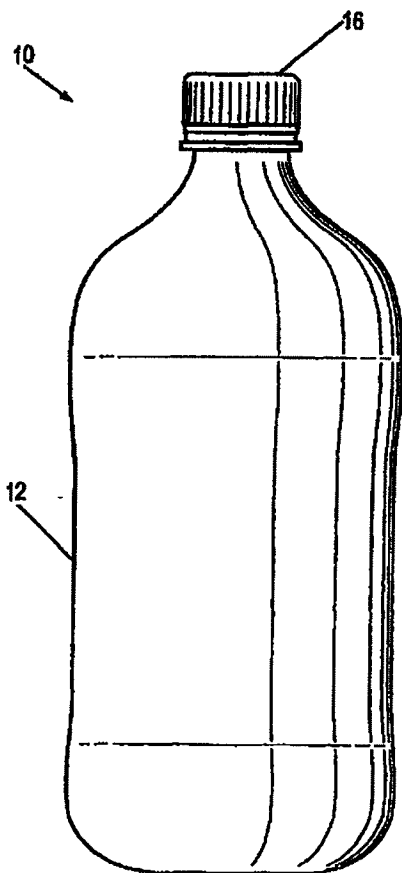
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(54) Title: **COATING COMPOSITION CONTAINING AN EPOXIDE ADDITIVE AND STRUCTURES COATED THEREWITH**



(57) Abstract: Coatings are provided to give polymeric structures a top coat that improves the gas barrier properties of the structure while enhancing the water resistance of the top coating and while improving the adhesion of the top coat to an underlying layer of the structure. These top coat compositions comprise an organic barrier coating material in combination with an epoxide additive which enhances the water resistance, adhesion, gas barrier, or a combination thereof, of the top coat barrier layer. Multilayer structures having this top coat are also provided, particularly in the form of containers for food and beverage packaging.

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COATING COMPOSITION CONTAINING AN EPOXIDE ADDITIVE AND STRUCTURES COATED THEREWITH

TECHNICAL FIELD

5 This invention relates to plastic films and containers, such as beverage containers, that include a barrier coating to reduce gas permeation therethrough, and more particularly to top coat materials for enhancing the performance properties of the barrier coating.

BACKGROUND OF THE INVENTION

10 Plastic containers comprise a large and growing segment of the food and beverage industry. Plastic containers offer a number of advantages over traditional metal and glass containers. They are lightweight, inexpensive, non-breakable, transparent, and easily manufactured and handled. Plastic containers have, however, at least one significant drawback that has limited their universal acceptance, especially
15 in the more demanding food applications. That drawback is that all plastic containers are more or less permeable to water, oxygen, carbon dioxide, and other gases and vapors. In a number of applications, the permeation rates of affordable plastics are great enough to significantly limit the shelf life of the contained food or beverage, or prevent the use of plastic containers altogether.

20 Plastic bottles have been constructed from various polymers, predominantly PET, for non-carbonated and particularly for carbonated beverages. All of these polymers, however, exhibit various degrees of permeability to gases and vapors, which have limited the shelf life of the beverages contained within them. For example, carbonated beverage bottles have a shelf life that is limited by loss of CO₂.
25 (Shelf life is typically defined as the time needed for a loss of seventeen percent of the initial carbonation of a beverage.) For non-carbonated beverages, similar limitations apply due to oxygen and/or water vapor diffusion. Diffusion means both ingress and egress (diffusion and infusion) to and from the bottle or container. It would be desirable to have a container with improved gas barrier properties.

30 A number of technologies have been developed to decrease the permeability of polymers, and thus increase their range of applicability to food and beverage packaging. (Permeability decrease is equivalent to barrier increase.) One of the most promising approaches has been the deposition of thin layers of inorganic oxides on the

surface of the polymers, either before or after mechanically forming the polymer into the finished container. See, e.g., PCT WO 98/40531. Inorganic oxides, especially silicon dioxide, have been explored extensively, because of their transparency, impermeability, chemical inertness, and compatibility with food and beverages.

- 5 Commercialization of containers based on polymeric/inorganic oxide multilayer structures, however, has been slow and mostly limited to flexible containers made by post-forming coated films.

In particular, rigid polymeric containers with inorganic oxide coatings have proven difficult to develop. Despite the relative ease of depositing inorganic oxides
10 onto the exterior surface of a rigid container, those containers have not exhibited sufficient reductions in permeability over the uncoated containers. This modest decrease in permeability is due to the presence of residual pinholes in the inorganic oxide layer. Pinholes are created, in part, by pressurization of containers—such as when containers hold carbonated beverages. The surface area occupied by these
15 pinholes is usually quite small (on the order of less than 1% of the total surface); however, the impact of these pinholes is far greater than their surface area would suggest, because diffusion through a polymer occurs in all three spatial dimensions. Each pinhole therefore can drain a much larger effective area of the container surface than the actual area of the pinhole.

- 20 Several methods have been explored to address the pinhole problem. The most common approach has been to deposit thicker layers of the oxide; however, this approach is inherently self-defeating. Thicker layers are less flexible and less extensible than thin layers, and therefore more prone to fracturing under stress. Another method is to apply multiple layers of inorganic oxides, sometimes with
25 intermediate processing to redistribute the pinhole-causing species. This approach also has met with little success, in part, because of the greater complexity of the process and because of its modest improvement in barrier performance. A third method has been to supply an organic sub-layer on the polymer surface to planarize the surface and cover up the pinhole-causing species prior to laying down the
30 inorganic oxide. This method also greatly increases the complexity and cost of the overall process, with only modest improvement in barrier performance. A fourth

approach has been to melt-extrude a second polymer layer on top of the inorganic oxide layer, in order to provide additional resistance to gas flow through the pinholes.

With this fourth approach, it has been reported that applying a 4 micron layer of poly(ethylene-co-vinyl acetate) on top of a PET/SiO_x structure improved the barrier property by 3x, and applying a 23 micron top layer of PET improved the barrier performance by 7x (Deak & Jackson, Society of Vacuum Coaters, 36th Annual Technical Conference Proceedings, p. 318 (1993)). Despite this barrier improvement, there has been little commercial implementation of this approach, for several reasons. First, melt extrusion of a second polymer onto a polymeric/inorganic oxide film imparts substantial thermal stress to the preformed structures, often severely compromising their barrier performance. Second, structures with two different polymers are inherently more difficult to recycle than structures composed of only one polymer. Third, co-extrusion of a second polymer onto preformed rigid containers is nearly impossible with current technology and is cost prohibitive for large volume applications in the food and beverage industry.

Yet another method has been fully explored to address this problem and has achieved promising results in barrier improvement. This method applies onto the inorganic oxide layer a top coat comprised of soluble organic compounds having a plurality of carboxyl, hydroxyl, or carboxamide functional groups. See, e.g., PCT WO 02/16484. This top coat blocks ingress or egress of gas or vapor through the pinholes and achieves a barrier improvement of 5 to 10 times or more, and improves the abrasion resistance of bottles coated with an inorganic oxide. One problem with these compounds, however, is their inherent water solubility. The top coat thus has a less than optimum water resistance. Some of the soluble compounds also do not adhere effectively to the inorganic oxide coating surface. It therefore would be advantageous to reduce or eliminate the problem of gas or vapor permeability through pinholes in the inorganic oxide layer of a multi-layered structure by providing a top coat layer that has improved adhesion to the inorganic oxide layers, good water resistance, and enhanced barrier performance.

Others have used UV-cured acrylic oligomers, organic solvent based epoxy-amine cured polymers, or halogenated organic formulations (e.g., polyvinylidene chloride) as barrier coatings or protective films for PET substrate/silica constructions.

It would be highly preferable to achieve the barrier and coating performance requirements described above with a water-based, essentially 100% VOC-free, and halogen-free coating composition.

It would therefore be desirable to provide barrier coated plastic structures having enhanced gas barrier properties and improved water resistance, particularly where the top coat exhibits good adherence to the underlying structure. It would also be desirable to provide compositions and methods for improved adhesion of a top coat barrier layer to a polymeric base layer or to an inorganic oxide layer, wherein the top coat fills any pinholes in the inorganic oxide layer and reduces the gas permeability of the multilayer structure. It would be further desirable to provide barrier coatings and methods that are water-based and substantially or completely free of volatile organic solvents and halogens.

SUMMARY OF THE INVENTION

Compositions and methods are provided to give polymeric structures a top coat that improves the gas barrier properties of the structure, while enhancing the water resistance of the top coating, and while improving the adhesion of the top coat to the underlying layer. These top coat compositions include an organic compound (barrier material) in combination with an epoxide additive that reacts with (e.g., crosslinks) the organic compound. The organic compound preferably is a water-soluble polymer, water-dispersible polymer, or aqueous emulsion polymer. Layered structures having this top coat are also provided, particularly in the form of containers for food and beverage packaging.

Containers employing the top coat meet the demanding requirements of most commercial applications. The containers demonstrate substantial water rinse resistance immediately after the top coat is dried, and coatings and bottles made with these coatings remain clear and adherent after more than 24 hours of soaking in room temperature water. Bottles having the coated structures described herein can provide a BIF of two or more, preferably five or more in the case of top coat on inorganic coating layer, even after abuse testing. For recycling purposes, the coatings can be removed during exposure to water at 80 °C at pH 12 or less. The coatings feel like PET plastic after water soak and are not slippery. They also can accept printing and

adhesives, and provide improved gloss on the containers. The coatings also possess good film mechanical properties to provide resistance to container handling abuse.

In preferred embodiments, the polymeric base layer is a thermoplastic polymer, particularly a polyester, such as polyethylene terephthalate (PET). The top coat comprises an organic compound capable of reducing the permeability of the gas barrier layer to gas or vapor, and an epoxide additive, which may cross-link the organic compound and/or which may react with neutralization agents in aqueous coating solutions. Desirably, the organic compound is polymeric. The organic compound preferably has a plurality of hydroxyl, carboxyl, amine, or carbonyl functional groups. Preferred organic compounds include polyvinyl alcohols and polyhydroxyaminoethers. The epoxide additive desirably undergoes a ring opening reaction with a functional group of the organic compound. Examples of suitable epoxide additives include, but are not limited to, resorcinol diglycidyl ether and glycerol diglycidyl ether.

In another aspect, methods are provided for reducing the permeability of vapor or gas through a polymeric structure comprising a polymeric base layer. The method steps include (i) applying to the polymeric base layer a solution, dispersion, or emulsion comprising an organic compound capable of reducing the permeability of the structure to gas or vapor, and an epoxide additive, to form a wet coating, and (ii) drying the wet coating, and reacting the epoxide additive, to form a top coat barrier layer on the structure. Optionally, an inorganic oxide barrier layer (e.g., a SiO_x coating) can be applied onto the polymeric base layer before applying the solution, dispersion, or emulsion to the polymeric base layer. This results in a multilayer structure with an inorganic oxide layer interposed between the polymer base layer and the top coat barrier layer.

The top coat solution, dispersion, or emulsion preferably is aqueous, and more preferably is substantially free of halogenated compounds and volatile organic solvents. The solution, dispersion, or emulsion typically is applied to the polymeric base layer or to the inorganic oxide barrier layer by using a spray coating, flowing, or dip coating technique. The drying and reacting preferably are conducted at a temperature less than or equal to about 75 °C.

In yet another aspect, methods are provided for packaging products, particularly foods and beverages. In a method of packaging a beverage, the steps include (i) providing a container comprising a polymeric container body; (ii) applying to an exterior surface of the polymeric container body a top coat comprising an organic compound capable of reducing the permeability of the container body to gas or vapor, and an epoxide additive; and (iii) depositing a beverage in the container. Such beverages desirably may be a carbonated beverage, such as a soft drink or beer, or a non-carbonated beverage, such as water or a juice-containing beverage.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is an elevation view of a packaged beverage including a container coated with a gas or vapor barrier top coat in accordance with an embodiment of this invention.

FIG. 2 is a partial sectional view of the container in FIG. 1 illustrating the multilayer structure of the container.

DETAILED DESCRIPTION OF THE INVENTION

A coated structure is provided which comprises a polymeric base layer, optionally an inorganic gas barrier layer on the surface of the polymeric base layer, and an improved top coat on the polymeric base layer or on the inorganic gas barrier layer. The top coat comprises an organic compound capable of reducing the permeability of the structure to gas or vapor, and an epoxide additive which enhances the water resistance, adhesion, gas barrier, or a combination thereof, of the top coat barrier layer, thereby providing a top coat with enhanced adhesion and/or improved water resistance. The top coat is particularly suitable for blocking ingress or egress of oxygen and carbon dioxide through polymeric packaging containers.

Composition for Forming the Top Coat

The coating compositions used for forming the top coat layer described herein preferably are provided as a solution, dispersion, or emulsion containing (i) an organic compound that provides a gas and vapor barrier, and (ii) an epoxide additive dispersed/dissolved therein which enhances the water resistance, the adhesion (i.e., promotion of adhesion to a polymeric base layer or to an intermediate inorganic barrier layer), the gas barrier, or a combination thereof, of the top coat barrier layer.

The solution, dispersion, or emulsion, which is preferably aqueous-based, must be capable of forming a continuous film upon drying.

In a particularly preferred embodiment, the aqueous solution, dispersion, or emulsion is at least substantially free of both volatile organic compounds (VOCs) and halogen compounds. As used herein, the term "at least substantially free" means in the case of a dispersion or emulsion that it contains no or only very low amounts of VOCs (i.e., less than 2% by weight VOCs) and in the case of a solution that it contains no or very low amounts of a low toxic organic solvent (i.e., less than 5% by weight). An example of a low toxic organic solvent is acetic acid.

10 The solution, dispersion, or emulsion preferably has a pH less than 7, more preferably less than 5.

The Organic Compound

The organic compound desirably is selected to reduce the permeability of the coated structure (to optimize barrier improvement) and should include one or more functional groups capable of bonding or reacting with the epoxide additive. Suitable organic compounds should have at least one, and preferably a plurality of, hydroxyl, carboxyl, carboxamide, amine, or carbonyl functional groups. The organic compound can be polymeric, oligomeric, or monomeric.

Preferred organic compounds include polyvinyl alcohols and polyhydroxyaminoethers. In a particularly preferred embodiment, the organic compound is a polyhydroxyaminoether (i.e., a hydroxy functionalized epoxy resin), such as BLOXTM (The Dow Chemical Company, Midland, Michigan, USA). BLOX 4000 Series Resins are particularly preferred, for their enhanced gas barrier properties. Examples of other suitable organic compounds include other polyetheramines and their salts, polyethyleneimines, polydextrose, polysaccharides, polyacrylic emulsions, emulsions, dispersions, and solutions of epoxy resins, urethane polymers, acrylic-urethanes, styrene-acrylic emulsions, and carboxy methyl cellulose.

Suitable organic compounds for forming the top coat are solid at temperature (25 °C) and pressure (atmospheric pressure). It is desirable that the organic compound for forming the top coat is non-toxic.

Although there are many solid/solvent combinations that are effective in the methods described herein, it is preferred that both the solid (i.e., the organic

compound) and solvent be compatible with food and beverages. It is particularly preferred that both the solid and solvent have regulatory approval for use in food-contact applications. It is especially preferred to use water as the solvent (or dispersion or emulsion medium), due to its low cost, non-toxicity, and ease of handling.

The Epoxide Additive

The epoxide additive is a monofunctional or multifunctional epoxide that enhances the water resistance, adhesion, and/or gas barrier properties of the organic compound of the top coat. While not being bound by any theory, it is believed that the epoxide works by either crosslinking the top coat material, thereby increasing the water resistance and adhesion of the top coat, or by reacting with neutralization agents present in aqueous coating solutions, dispersions, or emulsions, or by a combination of these mechanisms. Examples of these neutralization agents include acids, such as phosphoric acid, that are used to stabilize certain coating compositions, such as a dispersion of BLOX. It is believed that monofunctional epoxides operate solely by the latter mechanism, to reduce the water affinity of the organic coating, and thus enhance the water resistance of the organic coating layer.

The epoxide additive preferably comprises a multifunctional epoxide, which is an epoxide with two or more functional epoxide groups. For example, in a preferred embodiment, the epoxide additive is a bi-functional epoxide. In another embodiment, a epoxide additive includes a di-epoxide mixed with a small amount of a tri-epoxide. The epoxide should be at least partially soluble, dispersible, or emulsifiable in the organic compound or solvent of the coating emulsion, dispersion, or solution. The epoxide additive is believed to undergo a ring opening reaction with functional groups, such as amine or hydroxyl groups, of the organic compound in the coating solution, dispersion, or emulsion. This crosslinks the organic compound and forms a hard cross-linked polymer network, so that a tough film is formed when the coating is dried. The crosslinking reaction preferably is one that occurs to an appreciable extent at a low temperature, e.g., less than or equal to about 75 °C.

The cross-linking provides the top coat barrier layer with good water resistance—both to water at ambient (e.g., 22 °C) and elevated temperatures (e.g., up to 45 °C or higher). The degree of water resistance can be adjusted depending on the

application, for example, by altering the cross-linking density or the degree of cross-linking. This can be readily achieved by adjusting the ratio of the top coat organic compound (e.g., polymer) and the multifunctional epoxide additive, by adjusting the pH of the coating solution, dispersion, or emulsion, or by a combination of these approaches.

The cross-linked coating also can provide enhanced adhesion to the underlying substrate (e.g., PET), due to polar-polar attractions between the layers of materials. It is also possible to chemically react the epoxide to any available functional groups on the substrate surface, such as but not limited to, hydroxy and carboxyl functionality.

The barrier performance of the polymeric structure is improved by the top coat barrier layer, and the extent of that improvement depends, in part, on the thickness of the top coat. Generally, the thicker the coating layer, the greater the barrier to vapor and gas. The barrier of the coated containers can be varied for a particular application by varying the thickness of the top coat.

Structures having the top coat are potentially recyclable, as the top coat is lightly cross-linked and can be removed from the underlying polymeric layer or inorganic oxide layer using conventional techniques, such as caustic hot water baths.

Preferred epoxide additives include resorcinol diglycidyl ether and glycerol diglycidyl ether. Other suitable epoxide additives include polymeric epoxides, diethyleneglycol diglycidyl ether, polyethyleneglycol diglycidyl ether, glycerol polyglycidyl ether, diglycerol polyglycidyl ether, 1,2-epoxy butane, polyglycerol polyglycidyl ether, isoprene diepoxide, and cycloaliphatic diepoxide. Other representative examples of epoxide additives include 1,4-cyclohexanedimethanol diglycidyl ether, glycidyl 2-methylphenyl ether, glycerol propoxylate triglycidyl ether, 1,4-butanediol diglycidyl ether, sorbitol polyglycidyl ether, glycerol diglycidyl ether, tetraglycidyl ether of meta-xylenediamine, and diglycidyl ether of bisphenol A.

The epoxides of the epoxide additive can be water soluble or water insoluble. It can be solubilized as an emulsion or dispersion. Alternatively, it can be insoluble and dispersed in aqueous or nonaqueous liquids, emulsions, or combined with another dispersion in liquid.

The epoxide additive typically is added at a concentration of between 0.01 and 75 wt%, preferably between about 0.1 and 20 wt%, more preferably between about 0.5

and 7.5 wt %, based on the content of organic compound. In embodiments wherein the multi-functional epoxide additive is essentially insoluble or only marginally soluble in the liquid phase or emulsion or dispersion, then the lower limit is the solubility or saturation point in the coating mixture. The lowest usage limit of epoxide additives is the breakage of stability of epoxide in water either as solution or dispersion.

In preferred embodiments, the epoxide additive promotes adhesion between the organic coating layer and the base polymer layer. In preferred embodiments utilizing an inorganic oxide coating layer, the epoxide additive promotes adhesion between the organic coating layer and the inorganic oxide coating layer.

The Structure and Applying the Top Coat Thereto

The above described top coat compositions are useful in methods for enhancing the gas or vapor barrier properties of a monolithic polymeric structure having a polymeric base layer, or of a multilayer structure comprised of a polymeric base layer and an inorganic oxide gas barrier layer on a surface of the polymeric base layer.

In one embodiment, a container having a coated structure is made by the following steps: (i) providing a polymeric base layer, such as PET; (ii) applying to the base layer a solution, dispersion, or emulsion comprising the organic compound (barrier material) and an epoxide additive, to form a wet coating layer; and (iii) drying the wet coating layer to form a continuous, barrier enhancing top coat over and adhered to the polymeric base layer. In a preferred embodiment, the epoxide additive crosslinks with the organic compound.

In an alternative embodiment, a container having a multilayer structure is made by the following steps: (i) providing a polymeric base layer, such as PET; (ii) applying an inorganic gas barrier layer to the base polymer layer; (iii) applying to the inorganic gas barrier layer a solution, dispersion, or emulsion comprising the organic compound with epoxide additive to form a wet coating layer; and (iv) drying the wet coating layer and allowing the epoxide additive to crosslink with the organic compound to form a continuous, barrier enhancing top coat over and adhered to the inorganic gas barrier layer. In a preferred embodiment, the epoxide additive crosslinks with the organic compound.

In either approach, the steps, individually and in combination, can be conducted batchwise or in a continuous or semi-continuous process.

Polymeric Base Layer

The polymeric base layer preferably is a thermoplastic. Polyesters are particularly suitable, with polyethylene terephthalate (PET) being preferred for beverage packaging. Other suitable polyesters include polyethylene naphthalate (PEN), PET/PEN blends, PET copolymers, and the like. The base layer can be in the form of a flexible or rigid film or container. The coating compositions and methods described herein are most effective on substantially rigid containers, such as bottles.

Inorganic Barrier Layer

The optional inorganic gas barrier layer can be composed of silicon, silica, a metal (e.g., aluminum, Al), a metal oxide, or combination thereof. Silica (SiO_x) is particularly desirable for beverage containers because it is transparent, chemically inert, and compatible with food and beverages. The inorganic gas barrier layer preferably has a thickness between about 1 and about 100 nm.

The inorganic barrier coating can be applied to the polymeric base layer by a number of techniques. Examples of these techniques include sputtering and various types of vapor deposition, such as plasma vapor deposition, plasma enhanced chemical vapor deposition, and electron beam or anodic arc evaporative vapor deposition. Suitable vapor deposition techniques are described in U.S. Patent No. 6,279,505 to Plester, et al., and U.S. Patent No. 6,251,233, the disclosures of which are hereby expressly incorporated herein by reference. Alternatively, application of the inorganic oxide gas barrier layer can be conducted using a sol-gel process.

The Barrier Enhancing Top Coat

The top coat is applied to the inorganic barrier layer or polymer base layer to enhance the vapor or gas barrier of the structure. The top coat can be applied by dissolving the soluble organic compound in water or another suitable solvent, or by dispersing or emulsifying the organic compound in water or another liquid medium, and then applying the solution, dispersion, or emulsion to the inorganic barrier layer or polymer base layer using one of a variety of techniques known in the art. Examples of these coating techniques include dipping, flowing, or spraying. The application step may be followed by an optional step, such as spinning the coated bottle, to

remove excess coating material, if needed. Application of the top coat preferably includes this spinning step. Following application of the solution, dispersion, or emulsion, the epoxide additive reacts (e.g., crosslinks the organic compound, reacts with a neutralization agent) and the structure is allowed to dry such that the solvent
5 evaporates, causing the organic compound to precipitate and/or coalesce and form a film. In an embodiment having the optional inorganic oxide layer, when the solvent evaporates, the organic compound remains in the pinholes of the inorganic oxide barrier layer to block ingress or egress of gas or vapor. Preferably, the wet top coat is dried and crosslinked at a temperature less than or equal to about 75 °C (e.g., less than
10 60 °C, less than 50 °C, less than 40 °C, less than 30 °C, less than 25 °C). This low drying temperature (e.g., less than or equal to about 75 °C) is important because the polymeric base layer may shrink or deform when exposed to higher temperatures for an extended period of time, particularly for the preferred polymeric materials, and will cause the inorganic oxide coating layer, if present, to crack.

15 The thickness of the top coat may vary and can be very thin. Some top coats can be applied at a thickness of 50 microns or less and some can be applied at a thickness of 10 microns or less. Desirably, the top coat has a thickness of less than 5 microns. It should be understood, however, that the thickness of the top coat can be greater than 50 microns. The particular thickness of the top coat will be selected, in
20 part, based on the required barrier of the coated structure, as well as any barrier provided by other layers of the structure, e.g., whether an inorganic oxide layer is interposed between the top coat barrier layer and the polymeric base layer.

Forms and Uses of the Multilayer Structures

The top coat coatings and methods are particularly useful for enhancing the
25 gas or vapor barrier characteristics of containers such as food or beverage containers. The coatings and methods are particularly useful for enhancing the gas or vapor barrier characteristics of packaged food and beverage containers. The compositions and methods described herein preferably are used to form a coated plastic container comprising a plastic container body having an external surface and a coating on the
30 external surface of the container. The coating provides a barrier that inhibits the flow of gas into and out of the container, which is particularly useful in producing carbonated beverages. For example, the gas barrier coating can protect the beverage

from the flow of oxygen into the container from the outside or can inhibit the flow of carbon dioxide out of the beverage container. The resulting carbonated beverage has a longer shelf life because the coating on the container better holds the carbon dioxide within the container.

5 In the manufacture of packaged beverages, the top coat described herein can be applied to containers in a continuous packaged beverage manufacturing line between application of the inorganic oxide barrier layer to the container and filling the container with the beverage. Alternatively, the top coat possibly could be applied to the containers after they are filled with beverage. Regardless, the containers treated in
10 accordance with these compositions and methods described herein can be used to manufacture packaged beverages in a conventional packaged beverage manufacturing facility. Such beverages desirably may be a carbonated beverage, such as a soft drink, beer, or sparkling water; or a non-carbonated beverage, such as a juice-containing beverage or still water.

15 It is also envisioned that containers having the structure described herein would be useful for packaging oxygen-sensitive products, such as foods and beverages. For example, the enhanced barrier would reduce the flow of atmospheric oxygen into the container, thereby extending the shelf-life of an oxygen-sensitive product containing therein.

20 For embodiments having the underlying structure with the optional inorganic oxide barrier layer, a further benefit of the top coat compositions is that, in addition to enhancing the barrier properties of such structures, the top coat provides a method to increase the abuse resistance of such structures. Specifically, if film-forming polymeric materials are used as the organic compound, then deposition of those
25 polymers onto the surface of the inorganic oxide layer can increase the abuse resistance of that layer. This is particularly useful in manufacturing packaged beverages because of the necessary mechanical handling of the treated containers.

FIG. 1 illustrates a packaged beverage 10 comprising a container body 12, a beverage (not shown) disposed in the container, and a closure or cap 16 sealing the
30 beverage within the container body. FIG. 2 illustrates the multiple layers of the container body including the polymeric base layer 18, the inorganic oxide gas or vapor barrier layer 20 on the exterior surface 22 of the base layer, and a vapor or gas barrier

enhancing top coat 24 on the inorganic oxide barrier layer. Suitable polymers for forming the polymeric base layer 14 of the multilayer structure container 12 can be any thermoplastic polymer suitable for making containers, but preferably is PET. The inorganic oxide barrier layer 20 reduces the permeability of the container 10 to gas and vapor, particularly carbon dioxide and oxygen. The inorganic oxide barrier layer 20 suitably comprises a silica. The top coat 24, which includes an epoxide crosslinked with an organic compound, preferably a polymer, is applied so as to enhance the vapor or gas barrier of the multilayer structure container 12. The top coat 24 illustrated in the FIG. 2 is continuous on the surface of the inorganic oxide barrier coating, but can be discontinuous. The top coat 24 fills the pinholes 26 in the inorganic oxide gas barrier layer and reduces the permeability of the container 12 to gas or vapor.

In a preferred variation (not shown) of the structure illustrated in FIG. 2, the inorganic oxide barrier layer 20 is omitted, and the top coat barrier layer 24 is coated directly onto polymeric base layer 18.

The present invention will be further understood with reference to the following non-limiting examples.

EXAMPLES

In the following examples, PET bottles were subjected to various treatments that demonstrate the barrier-enhancing effect of the present compositions and methods. Barrier improvement and water resistance of the coating were assessed.

The barrier improvement factor (BIF) was determined by comparing the loss rates for containers with different coating compositions and layer structures. For example, the BIF of a plain, uncoated PET bottle is 1. Assuming the shelf life of a carbonated beverage packaged in a plain, uncoated PET bottle is about 10 weeks, the shelf life of a carbonated beverage in a coated PET bottle having a BIF of 1.2 would be about 12 weeks, the shelf life of a carbonated beverage in a coated PET bottle having a BIF of 2 would be about 20 weeks, and the shelf life of a carbonated beverage in a coated PET bottle having a BIF of 20 would be about 200 weeks. BIF can be measured using empty bottles with GMS (Gebele Measurement System) at 38 °C. In these examples, the CO₂ loss rate was measured by determining the rate that

CO₂ migrated to the exterior of the bottle, when the bottles were pressurized to 5 bar pressure and held at 38 °C.

Water resistance was determined by a variety of tests. Unless otherwise indicated in the individual examples described below, water resistance was measured by immersing the top coated bottles in ambient temperature (e.g., 22 °C) water for 24 hours, either 5 minute or 24 hours after the top coat was applied. The bottles then were rubbed continuously with firm finger pressure while immersed during the first 5 minutes of immersion. The appearance and feel of the coating was then observed. It was also determined whether any coating particles had dissolved into the water by, first, visually inspecting the water and bottle under light, and then comparing the weight of the coated bottles before and after the water resistance test. For example, when BLOXTM was used as the top coat, a white haze was observed in the water if the coating dissolved into the water. These tests were repeated every hour for the first five hours, and then again 24 hours after immersion. The top coat was considered water resistant (i.e., the coating passes the water resistance test) when (i) no coating can be rubbed off and no coating dissolves into the water following 24 hour immersion in water at 22 °C, and (ii) the coating of the bottles, while in the water, do not feel sticky.

Example 1: Water Resistance of PET Bottles Coated With BLOXTM and Resorcinol Diglycidyl Ether

Resorcinol diglycidyl ether ("RDGE"), which is one of the monomer components of BLOXTM and is sparsely soluble/dispersible in a dispersion of BLOXTM, was used as a multifunctional epoxide additive. After 4 hours of mixing the 1.5wt% of RDGE and 20wt% of BLOXTM water dispersion (i.e., 98.5 wt% BLOX dispersion consisting of 20.0 wt% polymer solids and the balance water) at PH less than 5, PET bottles were coated by pouring the mixture on the bottles while the bottles were rotating, and then spinning off the excess materials from the bottles and dried at 60 °C for two minutes in a temperature-controlled oven. The coating thickness achieved in this manner was around 1.5 to 2.0 µm. The bottles were then tested for water resistance (WR). The coated bottles passed all of the WR tests.

Example 2: Removability of BLOXTM and Resorcinol Diglycidyl Ether Coating from PTE Bottles

**Example 10: Comparative Example—BLOXTM Coating on
SiO_x-Coated PET Bottles With No Epoxide Additive**

A BLOXTM dispersion without any additives was coated onto SiO_x-coated PET bottles and dried either at 60 °C for 2 minutes in a temperature controlled oven
5 or with hot air at 66 °C. A coating thickness of around 1.5 to 2.0 µm was achieved. The bottles were then tested for water resistance; they failed, as the top coating dissolved in water, irrespective of the drying method used.

**Example 11: Water Resistance of SiO_x-Coated PET Bottles Coated
with BLOXTM and 1,2-Epoxy Butane**

10 PET bottles were made and coated with a thin layer of an inorganic oxide, SiO_x. A dispersion of 1.5wt% of 1,2-epoxy butane, a monofunctional epoxide additive, and 20wt% of BLOXTM in water (i.e., 98.5 wt% BLOX dispersion consisting of 20.0 wt% polymer solids and the balance water) was prepared and then coated onto SiO_x-coated PET bottles by pouring the mixture on the bottles while the bottles were
15 rotating, spinning excess materials off the bottles, and then drying the BLOX/SiO_x-coated bottles at about 66 °C. A coating thickness of around 1.5 to 2.0 µm was achieved. The multilayer-coated bottles then were subjected to, and passed, all WR tests.

Example 12: Comparative Example—Water Resistance of SiO_x-Coated

20 **PET Bottles Coated With Acetic Acid-Containing BLOXTM
Dispersion and No Epoxide Additive**

PET bottles were made and coated with a thin layer of an inorganic oxide, SiO_x. A milky white dispersion containing 0.5wt% acetic acid, plus another mineral acid, and 20wt% BLOXTM was prepared. Then, the SiO_x-coated PET bottles were
25 coated with the dispersion by dip coating them in the dispersion, draining and then spinning them to remove excess coating. The bottles were then dried in a forced air oven at 60 °C for two minutes. A coating thickness of around 1.5 to 2.0 µm was achieved. Five minutes later, the coated bottles were immersed in room temperature water for 15 minutes and rubbed as in the water resistance test described in Example
30 1.

Next, the bottles were subjected to a harsher adhesion test to determine if a freshly coated bottle can retain the coating in water at an elevated temperature. The

bottles were immersed in water at 45 °C. It was observed that the coating came off, as evidenced by the water turning cloudy.

**Example 13: Water Resistance of SiO_x-Coated PET Bottles Coated
With Acetic Acid-Containing BLOX™ Solution
and Resorcinol Diglycidyl Ether**

PET bottles were made and coated with a thin layer of an inorganic oxide, SiO_x. A viscous solution containing 4wt% acetic acid and 20wt% BLOX™ was prepared, and, due the viscosity, diluted to 3-8wt% BLOX before use. A coating mixture was prepared from the diluted solution (98.5wt%) and resorcinol diglycidyl ether (RDGE) (1.5wt%). Then, the SiO_x-coated PET bottles were coated with the coating mixture by dip coating them in the mixture, draining and then spinning them to remove excess coating. The bottles were then dried. A coating thickness of around 1.5 to 2.0 µm was achieved. Water resistance tested were conducted on the bottles as described in Example 12. It was observed that the coating remained on the bottle, as evidenced by no clouding of the 45 °C water.

**Example 14: Water Resistance of SiO_x-Coated PET Bottles Coated
With Acetic Acid-Containing BLOX™ Solution
and Sorbitol Polyglycidyl Ether**

SiO_x-coated PET bottles were made and top coated as described in Example 12; however, sorbitol polyglycidyl ether (SPGE) (1.5wt%) rather than RDGE was used as the epoxide additive. The coating was 8.0wt% BLOX. A coating thickness of around 1.5 to 2.0 µm was achieved. The top coated bottles were subjected to, and passed, the water resistance tests described in Example 12.

**Example 15: Water Resistance of SiO_x-Coated PET Bottles Coated
With Acetic Acid-Containing BLOX™ Solution
and Diglycidyl Ether of Bisphenol A**

SiO_x-coated PET bottles were made and top coated as described in Example 12; however, a 65wt% dispersion of diglycidyl ether of bisphenol A (DGEBA) (2.3wt%) rather than RDGE was used as the epoxide additive. The coating was 8.0wt% BLOX. A coating thickness of around 1.5 to 2.0 µm was achieved. The top coated bottles were subjected to, and passed, the water resistance tests described in Example 12.

**Example 16: Water Resistance of SiO_x-Coated PET Bottles Coated
With Acetic Acid-Containing BLOXTM Solution
and 1,4-Butanediol Diglycidyl Ether**

SiO_x-coated PET bottles were made and top coated as described in Example
5 12; however, 1,4-butanediol diglycidyl ether (BDGE) (1.5wt%) rather than RDGE
was used as the epoxide additive. The coating was 8.0wt% BLOX. A coating
thickness of around 1.5 to 2.0 μm was achieved. The top coated bottles were
subjected to, and passed, the water resistance tests described in Example 12.

**Example 17: Water Resistance of SiO_x-Coated PET Bottles Coated
10 With Acetic Acid-Containing BLOXTM Solution
and Glycerol Diglycidyl Ether (1.2%)**

SiO_x-coated PET bottles were made and top coated as described in Example
12; however, glycerol diglycidyl ether (GDE) (1.2wt%) rather than RDGE was used as
the epoxide additive. The coating was 6.0wt% BLOX. A coating thickness of around
15 1.5 to 2.0 μm was achieved. The top coated bottles were subjected to, and passed, the
water resistance tests described in Example 12.

**Example 18: Water Resistance of SiO_x-Coated PET Bottles Coated
With Acetic Acid-Containing BLOXTM Solution
and Glycerol Diglycidyl Ether (0.6%)**

20 SiO_x-coated PET bottles were made and top coated as described in Example
12; however, GDE (0.6wt%) rather than RDGE was used as the epoxide additive.
The coating was 3.0wt% BLOX. A coating thickness of around 1.5 to 2.0 μm was
achieved. The top coated bottles were subjected to, and passed, the water resistance
tests described in Example 12.

**Example 19: Water Resistance of SiO_x-Coated PET Bottles Coated
25 With Acetic Acid-Containing BLOXTM Solution
and Tetra Glycidyl Ether of Meta-Xylenediamine**

SiO_x-coated PET bottles were made and top coated as described in Example
12; however, tetra glycidyl ether of meta-xylenediamine (GEX) (1.5wt%) rather than
30 RDGE was used as the epoxide additive. The coating was 8.0wt% BLOX. A coating
thickness of around 1.5 to 2.0 μm was achieved. The top coated bottles were
subjected to, and passed, the water resistance tests described in Example 12.

Example 20: Barrier Improvement of PET Bottles Coated With BLOX™ With and Without Epoxide Additive

PET bottles were prepared and coated with a BLOX™ top coat (20%) containing a resorcinol diglycidyl ether additive, a glycerol diglycidyl ether additive, or no additive. A coating thickness of around 1.5 to 2.0 μm was achieved. The bottles were then tested for barrier improvement factor (BIF) relative to uncoated PET bottles. The results are shown in Table 1.

Table 1: BIF Comparison of Various Coating Structures

Bottle Structure	BIF
PET	1
PET + 20% BLOX™ (1.7 μm thick)	1.91
PET + 20% BLOX™ + 1.5% resorcinol diglycidyl ether	1.96
PET + 20% BLOX™ + 1.5% glycerol diglycidyl ether (about 3 μm thick)	2.03

For comparison purposes, BIF values were calculated for the PET bottles having other layer thicknesses of BLOX™ coating. These structures and BIF values are shown in Table 2.

Table 2: BIF Comparison of Various BLOX™ Coatings

Bottle Structure	BIF
PET (28 g bottle)	1
PET + 1.75 micron BLOX™	1.91
PET + 2.5 micron BLOX™	2.1
PET + 3 micron BLOX™	2.3
PET + 4 micron BLOX™	2.7
PET + 5 micron BLOX™	3.1

Example 21: Barrier Improvement of SiO_x-Coated PET Bottles Coated With BLOX™ With and Without Epoxide Additive

SiO_x-coated PET bottles were prepared and top coated with a BLOX™ top coat (20%) containing a resorcinol diglycidyl ether (RDGE) additive, a glycerol diglycidyl ether (GDE) additive, or no additive. The bottles were coated as in Example 6, and a coating thickness of around 1.5 to 2.0 μm was achieved. The bottles were then tested

for barrier improvement factor (BIF) relative to non-top coated, SiO_x-coated PET bottles. The results are shown in Table 3.

Table 3: BIF Comparison of Various Coating Structures

Bottle Structure	BIF
SiO _x -Coated PET	1.76
SiO _x -Coated PET + 20% BLOX TM	6.63
SiO _x -Coated PET + 20% BLOX TM + 1.5% GDE	6.63
SiO _x -Coated PET + 20% BLOX TM + 1.5% RDGE	6.81

- 5 These results of these Examples indicate that the inclusion of an epoxide additive in the organic top coat can enhance the water resistance and adhesion of the organic top coat while improving the overall BIF of containers therewith, as compared with bottles having organic barrier coatings alone or with bottles having organic barrier coatings in combination with inorganic barrier coatings. The epoxide additive has been shown to effect the combination of improvements.

Those skilled in the art will recognize, or be able to ascertain using no more than routine experimentation, many equivalents to the specific embodiments of the invention described herein. The references cited herein are hereby incorporated by reference.

WE CLAIM:

1. A coated structure comprising:

a polymeric base layer; and

a top coat barrier layer coated on the polymeric base layer, the top coat barrier layer comprising an organic compound capable of reducing the permeability of the structure to gas or vapor, and an epoxide additive which enhances the water resistance, adhesion, gas barrier, or a combination thereof, of the top coat barrier layer,

wherein the epoxide additive is selected from the group consisting of 1,4-cyclohexanedimethanol diglycidyl ether, glycidyl 2-methylphenyl ether, glycerol propoxylate triglycidyl ether, 1,4-butanediol diglycidyl ether, sorbitol polyglycidyl ether, glycerol diglycidyl ether, tetraglycidyl ether of meta-xylenediamine, and diglycidyl ether of bisphenol A.

2. A coated structure comprising:

a polymeric base layer; and

a top coat barrier layer coated on the polymeric base layer, the top coat barrier layer comprising an organic compound capable of reducing the permeability of the structure to gas or vapor, and an epoxide additive which enhances the water resistance, adhesion, gas barrier, or a combination thereof, of the top coat barrier layer,

wherein the organic compound is selected from the group consisting of polyvinyl alcohols, polydextrose, polysaccharides, epoxy resins, urethane polymers, polyethyleneimines, acrylic urethanes, and styrene acrylics.

3. A method for reducing the permeability of vapor or gas through a structure comprising a polymeric base layer, the method comprising:

applying to the polymeric base layer a solution, dispersion, or emulsion, which comprises (i) an organic compound capable of reducing the permeability of the structure to gas or vapor, and (ii) an epoxide additive, to form a wet coating, said applying comprising a spray coating or dip coating technique; and

drying the wet coating to form a top coat barrier layer on the structure, wherein the epoxide additive enhances the water resistance, adhesion, gas barrier, or a combination thereof, of the top coat barrier layer.

4. A method for reducing the permeability of vapor or gas through a structure comprising a polymeric base layer, the method comprising:

applying to the polymeric base layer a solution, dispersion, or emulsion, which comprises (i) an organic compound capable of reducing the permeability of the structure to gas or vapor, and (ii) an epoxide additive, to form a wet coating; and

drying, at a temperature greater than 66 °C to about 75 °C, the wet coating to form a top coat barrier layer on the structure, wherein the epoxide additive enhances the water resistance, adhesion, gas barrier, or a combination thereof, of the top coat barrier layer.

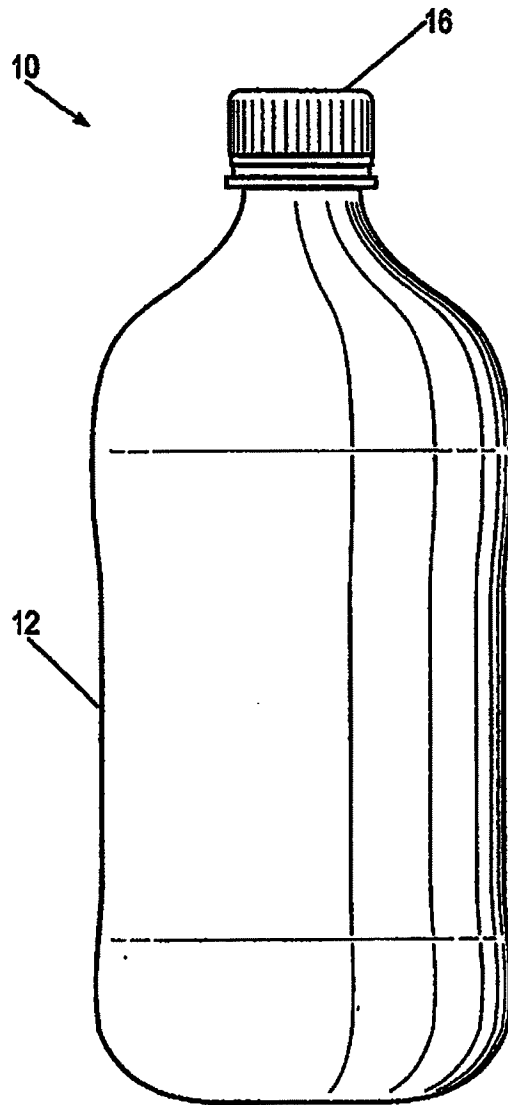


Fig. 1

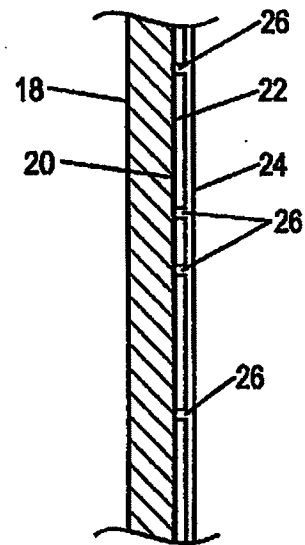


Fig. 2

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 7 C08J7/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08J B65D B32B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2 836 318 A (ADAKONIS ALBERT E ET AL) 27 May 1958 (1958-05-27) example 1A	1,4
X	US 5 300 541 A (NUGENT JR RICHARD M ET AL) 5 April 1994 (1994-04-05) column 1-3; example 1	2-4
X	FR 1 173 372 A (PLAX CORP) 24 February 1959 (1959-02-24) page 3; example 3	1,3,4
X	WO 96 18669 A (PPG INDUSTRIES INC) 20 June 1996 (1996-06-20) page 24-25; examples	1
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Further documents are listed in the continuation of box C.



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Date of the actual completion of the international search

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 02 16484 A (COCA COLA CO) 28 February 2002 (2002-02-28) the whole document -----	1-4

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 2836318	A	27-05-1958	CH 384208 A	15-11-1964
			DE 1150481 B	
			FR 1209460 A	02-03-1960
US 5300541	A	05-04-1994	US 5008137 A	16-04-1991
			US 5489455 A	06-02-1996
			US 5438109 A	01-08-1995
			US 5491204 A	13-02-1996
			US 5573819 A	12-11-1996
			CA 1337137 C	26-09-1995
			DE 68928668 D1	18-06-1998
			DE 68928668 T2	26-11-1998
			EP 0327039 A2	09-08-1989
			ES 2116261 T3	16-07-1998
			JP 2004820 A	09-01-1990
			JP 2057215 C	23-05-1996
			JP 7091368 B	04-10-1995
			MX 166278 B	28-12-1992
			MX 9205371 A1	31-03-1994
FR 1173372	A	24-02-1959	US 2830721 A	15-04-1958
			BE 556094 A	
			CH 360494 A	28-02-1962
			GB 842905 A	27-07-1960
			NL 215804 A	
WO 9618669	A	20-06-1996	AT 186930 T	15-12-1999
			AU 3679995 A	03-07-1996
			CA 2206898 A1	20-06-1996
			DE 69513538 D1	30-12-1999
			DE 69513538 T2	18-05-2000
			EP 0797608 A1	01-10-1997
			ES 2141387 T3	16-03-2000
			WO 9618669 A1	20-06-1996
			US 5637365 A	10-06-1997
WO 0216484	A	28-02-2002	AU 8660301 A	04-03-2002
			CA 2419370 A1	28-02-2002
			EP 1311595 A2	21-05-2003
			WO 0216484 A2	28-02-2002

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(54) Title: PRINTABLE HIGH BARRIER MULTILAYER FILM (57) Abstract A film combination comprising a) an oriented polymeric substrate which either i) comprises an intimate blend of polypropylene with maleic acid anhydride modified polypropylene or ii) is otherwise susceptible of transmitting oxygen and water vapor and has a primer coating on at least one surface; b) a layer of cross-linked polyvinyl alcohol on i) the intimate blend or ii) the primer coating; c) a layer of a polymer comprising vinyl alcohol residues which may be as defined in b) or an intimate blend of a homo- or copolymer of vinyl alcohol, with an ethylene acrylic acid copolymer; and, optionally d) a layer as defined in a)i).		

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PRINTABLE HIGH BARRIER MULTILAYER FILM

This invention relates to a multilayer packaging film having good barrier resistance to the transmission of oxygen and water vapor, good printability; and the ability to receive a firmly bonded metal layer thereon.

Certain polymeric films e.g., polypropylene, employed for the packaging of foods, inherently permit the transmission of oxygen and water vapor from outside of the film to inside of a package made up of the film. Oxygen and water vapor permits rapid deterioration of foods packaged in containers made from such a film. Metal deposits on such films are desirable because of the improvement in appearance and in providing yet another layer which militates against the invasion of oxygen and water vapor.

Thus, it is a principal object of the present invention to present a film which has excellent printability, can have a metal layer firmly bonded thereto and which has significantly decreased oxygen and water vapor transmission rates.

According to one aspect of this invention, there is provided a film combination comprising:

(a) an oriented polymeric substrate which either i) comprises an intimate blend of polypropylene with maleic acid anhydride modified polypropylene or ii) is otherwise susceptible of transmitting oxygen and water vapor and has a primer coating on at least one surface;

(b) a layer of cross-linked polyvinyl alcohol on i) the intimate blend or ii) the primer coating;

(c) a layer of a polymer comprising vinyl alcohol residues which may be as defined in b) or an intimate blend of a homo- or copolymer of vinyl alcohol, with an ethylene acrylic acid copolymer; and, optionally

(d) a layer as defined in a)i).

This invention is also concerned with a film combination comprising:

(a) an oriented polymeric substrate susceptible in its unmodified form of transmitting oxygen and water vapor;

(b) a primer coating on at least one surface of said substrate (a);

(c) a layer of cross-linked polyvinyl alcohol on said coating (b); and

(d) a layer of the blend of (1) a polyvinyl alcohol homo or copolymer and (2) an ethylene-acrylic acid copolymer.

It is preferred that the substrate layer be corona discharge treated prior to receipt of the primer coating.

The present invention also relates to a process for forming a firmly bonded film combination comprising:

(a) preparing an intimate blend of polypropylene and a maleic acid anhydride modified polypropylene and forming a cast layer thereof;

(b) forming said cast layer into a machine direction oriented film;

(c) applying a coating of poly(vinyl alcohol) containing cross-linking means to the machine direction oriented film;

(d) mating a second so-coated machine direction oriented film so that poly(vinyl alcohol) surfaces are in contact;

(e) transverse direction orienting the mated films to form a film combination of high delamination resistance.

The invention is also concerned with a film combination comprising:

(a) a pair of films each comprised of an intimate blend of polypropylene and a maleic acid anhydride modified polypropylene;

(b) coatings of poly(vinyl alcohol) containing cross-linking means having been applied to a surface of each of said pair while said pair had been in a machine direction orientation condition; and

(c) each coated film having been positioned with the poly(vinyl alcohol) layers in intimate contacting relationship while said coated contacting films had been transverse direction oriented.

The substrates contemplated herein include any polymeric film substrate which inherently permits the transmission of oxygen and water vapor and wherein the utility of such film for packaging purposes would call for a minimization of such transmission. In most cases the source of oxygen and water vapor is atmospheric oxygen and water vapor. While nylon, polyethylene terephthalate and polycarbonate films are contemplated herein, the particularly preferred class of films are the polyolefins. Within the polyolefins class, homopolymer and copolymers of propylene are preferred. Particularly preferred are isotactic polypropylenes containing at least 80% by weight of isotactic polypropylene. The preferred base substrate layer can be homopolypropylene having a melting point from 305 to 340°F, preferably from 321° to 336°F; an inherent viscosity from 1.4 to 4.0; an MFI from 0.5 to 12; an MW from 100,000 to 600,000; and a density from 0.89 to 0.91. Commercially available materials of this description include Exxon 4252 and ARCO W472. The preferred substrate can also be coextruded with a thin skin layer amounting from about 2-12% of the total

thickness of a copolymer of propylene and another olefin, e.g., ethylene, butene-1, etc. The other olefin can be present in the copolymer in an amount from about 1-7 wt%.

5 This invention encompasses polypropylene substrates comprising from (90 to 99 wt%, preferably from 92.5 to 98.5 wt%, of a polypropylene resin as described herein, compounded with or modified by from (1 to 10 wt%, preferably from 1.5 to 7.5 wt%, based on
10 the weight of the polypropylene resin of a maleated polypropylene.

 The maleated polypropylene additive may be derived from maleic acid or its anhydride, copolymerized with polypropylene. Pertinent properties of maleated
15 polypropylene marketed by Eastman Chemical are as follows:

 Ring and Ball softening 157°C;
 M.W. 4500;
 Density °C 0.934;
20 Acid Number 45;
 Brookfield Visc. 190°C.cp/370
 Color Gardner Scale 11;
 Penetration Hardness, 100 gm/5 sec./25°C
 tenths of mm.0-1.

25 In addition, the term maleic anhydride modified polypropylene homopolymer is the product resulting from the reaction between maleic anhydride and the thermal degradation product of polypropylene. Examples of this material can be found disclosed in U.S. 3,480,580.

30 In order to effectively inhibit the amount of oxygen and water vapor transmitted through the base layer, the base layer should preferably be (1) treated to a surface free energy of at least about 35 dynes/cm, (2) have a primer coating applied thereto, (3) have a
35 coating of a layer of a cross-linked polyvinyl alcohol

homopolymer or copolymer applied thereto, and (4) have a layer of a blend of a polyvinyl alcohol homo or copolymer and a ethylene-acrylic acid copolymer applied thereto.

5 The preferred substrate must be properly prepared to receive the primer layer, followed by application of the cross-linked polyvinyl alcohol. This proper treatment involves treating the surface to a surface tension level of at least about 35 and preferably from 10 38 to 45 dynes/cm in accordance with ASTM Standard D2578-84. The treatment can be flame treatment, plasma treatment, chemical treatment or corona discharge treatment. Flame treatment and corona discharge treatment are preferred with corona discharge treatment 15 being particularly preferred.

 Commercially available corona discharge treatment equipment can be obtained from Solo Systems, Inc., Garland, Texas; Corotec Corporation, Collinsville, Connecticut; Softal Electronics, Hamburg, W. Germany; 20 and others. Using, for example, Softal Electronics equipment, a treater can have an air gap of about 0.050 in. when treating polypropylene film of about 0.9 mils. The film can be treated to 42-44 dynes/cm. After this treatment, a suitable primer material may be coated 25 onto the treated surface.

 Preferred primer materials are those disclosed in U.S. 4,564,559. These include a primer produced by condensing a monoaldehyde with an interpolymer of acrylamide or methacrylamide and at least one other 30 unsaturated monomer. Further included is a material resulting from condensing aminoaldehyde with acrylamide or methacrylamide and subsequently interpolymerizing the condensation product with at least one other unsaturated monomer in the presence of a C_1-C_6 alkanol. 35 A preferred primer coating resin of this type comprises

5 a copolymer containing up to 90% by weight of styrene,
up to 80% by weight of an alkyl alkylate, up to 15% by
weight of methacrylic acid and 5% to 25% by weight of
acrylamide which has been condensed with a solution of
10 formaldehyde in n-butanol containing from 0.2 to 3
equivalents of formaldehyde for each amine group in the
copolymer. Another primer resin of this type is a 50%
solid solution of a copolymer resin containing 38.5
parts of styrene, 44 parts of ethyl acrylate, 2.5 parts
10 of methacrylic acid and 15 parts of acrylamide which
has be condensed with 5.2 parts of formaldehyde in
n-butanol.

15 A particularly preferred primer material for the
structure contemplated herein has been found to be
poly(ethyleneimine). The amine primer provides an
overall adhesively active surface for thorough and
secure bonding with the subsequently applied
cross-linked polyvinyl alcohol. It has been found that
20 an effective coating solution concentration of the
poly(ethyleneimine) applied from either aqueous or
organic solvent media, such as ethanol, is a solution
comprising 0.1 to 0.6% by weight of the
poly(ethyleneimine). A commercially available material
of this type is known as Polymin P, a product of
25 BASF-Wyandotte Corporation.

Another particularly preferred primer material is
the reaction product of an epoxy resin with an
acidified aminoethylated vinyl polymer. The
contemplated epoxy resins are glycidyl ethers of
30 polyhydroxy compounds. Typical polyhydroxy compounds
which may be used include bisphenol A, ring-substituted
bisphenol A, resorcinol, hydroquinone,
phenol-formaldehyde, Novolac resins, aliphatic diols,
such as ethylene glycol, propylene glycol,
35 1,4-butanediol, 1,6-hexane-diol, glycerol, lower alkyl

hydantoins and mixtures thereof. The preferred epoxy resins of the present invention are those made by the glycidation reaction between epichlorohydrin and bisphenol A. Epoxy resins of this type are commonly classified by their epoxy equivalent weight (EEW) which is defined by the weight of resin in grams which contains one gram equivalent of epoxy groups. Resins with an EEW ranging from 170 to 280 may be used in the present invention, but the preferred range is 180 to 210.

Although the specific structure of the epoxy resin is not critical to the primer employed in the present invention, important considerations in the selection of the epoxy resin revolve around its physical state. For example, it must be liquid and capable of being readily dispersed or dissolved with the second component or curing agent as described hereinbelow. If the epoxy resin is of low viscosity, it may be stirred directly into the second component, i.e., curing agent, however, it is preferred to employ the epoxy resin in an aqueous emulsion.

The second component in the epoxy primer composition of the present invention is an amino modified acrylic polymer which is water soluble. This polymer is a curing agent for the epoxy compound. The preferred material is described in U.S. 3,719,629. This material may be generically described as an acidified aminoethylated interpolymer having pendent aminoalkylate groups. This material is produced by polymerizing acrylate, methacrylate, styrene or other suitable monomers with sufficient methacrylic or acrylic acids to give a -COOH content of 7.5 to 12.5%. Solvent polymerization techniques are preferred. The polymer is then reacted with ethyleneimine monomer and

acidified with hydrochloric acid to render the polymer water soluble.

In one embodiment of the present invention, a liquid epoxy resin is emulsified in a solution of the curing agent by rapid stirring, the resultant dispersion is diluted with water to the desired concentration for coating, usually from 2 to 20% solids. When mixing the epoxy resin with the curing agent, it is generally preferred to use a stoichiometric equivalent balance of epoxy and amine groups. However, it has been found that the stoichiometric ratio may be varied over a wide range, from 1 epoxy to 3 amine groups through 3 epoxy groups to 1 amine group.

The polyvinyl alcohol employed herein can be any commercially available material. For example, ELVANOL 71-30, an E. I. DuPont product. The polyvinyl alcohol coating solution is prepared by dissolving the polymer in hot water, cooling and mixing both with a suitable cross-linking agent and an acid catalyst. The cross-linking agent can be a melamine- or urea-formaldehyde resin. Commercially available cross-linkers also would include PAREZ 613, a methylated melamine formaldehyde; CYMEL 373, a methylated melamine formaldehyde; CYMEL 401, a trimethylol melamine urea formaldehyde; glyoxal, borax, etc. An acid catalyst, e.g., ammonium sulfate, ammonium chloride, sulfuric acid, nitric acid and ammonium nitrate will effectively catalyze these systems.

Cross-linking is carried out to make the polyvinyl alcohol less moisture sensitive but it is essential that this does not occur before the coating weight is applied and evenly distributed. This is effected by making up the aqueous solution so that the initial

concentration is too low for this to occur but, as drying occurs, the concentration increases and the rate of cross-linking is heightened.

Suitable concentrations have been found to be from 3 to 10, preferably from 4 to 8 wt% of the solution being polymer plus cross-linking agent plus catalyst. If the solids content is higher, the solution becomes too viscous; if lower, good water resistance is not obtained. From 10% to 30%, typically 15% cross-linking agent is used with from 0.5% to 4.5%, typically 2% of the acid catalyst. A preferred formulation comprises the following solids content: 85.5 wt% polyvinyl alcohol; 12.8 wt% methylated melamine formaldehyde; and 1.7 wt% ammonium chloride (NH_4Cl).

The aqueous polyvinyl alcohol solution was prepared by dissolving sufficient ELVANOL 71-30 in hot water to form an 8 wt% solution which was then cooled. To this solution was added a 20 wt% aqueous melamine formaldehyde solution and a 5 wt% aqueous ammonium chloride solution to provide the preferred formulation recited above.

By cross-linking the underlying layer of polyvinyl alcohol, the moisture resistance of the polyvinyl alcohol is dramatically improved. The over-lying blend layer of polyvinyl alcohol and ethylene-acrylic acid copolymer provides a surface that is excellently printable and metallizable.

The final layer of the multilayer film structure is made up of a blend of noncross-linked polyvinyl alcohol homopolymer or copolymer and ethylene-acrylic acid copolymer. The polyvinyl alcohol is the same polyvinyl alcohol as described above. The ethylene acrylic acid copolymer is produced by the high pressure copolymerization of ethylene and acrylic acid. When ethylene is copolymerized with acrylic acid, the

molecular structure is significantly altered by the random inclusion of bulky carboxylic acid groups along the back-bone and side chains of the copolymer. The carboxyl groups are free to form bonds and interact with any polar substrate. They can also hydrogen bond together to yield toughness. The carboxyl groups tend to inhibit crystallization which results in clarity, low melting and softening point for the film. The ethylene-acrylic acid copolymers consist essentially of about 96 mol% methylene groups, thus, their water resistance is understandably similar to that of polyethylene. The ammonium salts of the copolymers permit water dispersions of the material to be formed which facilitates ease of topical application to surfaces. These copolymers can be formed having melt indexes from 300 to 3,000. Commercially available examples of these copolymers are PRIMACOR 4983 (Dow Chemical Co.) an aqueous dispersion having 25% solids content and obtained from a reaction between approximately 15 mol% acrylic and a 5 mol% ethylene; and Michem 4983 available from Michaelman Corporation.

In preparing the blend of the polyvinyl alcohol homopolymer or copolymer and the ethylene-acrylic acid copolymer, the components can range from 1:2 to 2:1 by weight. In preparing a roughly 2:1 blend in an aqueous dispersion for example, 10 parts of Vinol 325 (a 98% hydrolyzed medium viscosity polyvinyl alcohol, obtained from Air Products) can be mixed with 90 parts by weight of Michem 4983 (an ethylene-acrylic acid copolymer obtained from Michaelman Corporation). The Michem 4983 has a solids content of about 25%. This combination, adjusted to an aqueous 5% solid solution will provide the polyvinyl alcohol to ethylene-acrylic acid copolymer mixture in a ratio of approximately 2:1.

A metal layer, for example one comprising aluminium, may be deposited on the intimate blend of layer (c).

The following Examples illustrate the invention.

EXAMPLE 1

A homopolymer polypropylene film with a biaxial orientation from 4 to 5 times MD and from 7 to 10 times TD was corona discharge treated to a wetting tension of about 42 dynes/cm. The treated film was precoated on both sides with 0.1 wt% poly(ethyleneimine), i.e. Polymin M, a product of BASF-Wyandotte Corp. The film was air-dried at a 100°C. This coating weight was too low to be measured but is calculated to be in the range of 0.001 grams per 1000 in². A commercially available acrylic heat seal layer is applied to one side. The opposite surface of the film structure was coated with a formulation comprising 85.5 wt% polyvinyl alcohol, 12.8 wt% methylated melamine formaldehyde and 1.7 wt% ammonium chloride. The solution was applied utilizing a reverse direct gravure coater and the coated film was passed through a dry-air oven at from 100-125°C. This produced a coating wt of 0.5 g/m². After allowing the polyvinyl alcohol 3 days to partially cross-link, the film was recoated with the polyvinyl alcohol/ethylene-acrylic acid copolymer mixture. The coating weight of this mixture was 0.05 g/msi. The following table shows oxygen transmission data and ink adhesion data.

TABLE

	<u>Ink</u>	<u>Ink Pick-off</u>	<u>Oxygen Transmission</u>		
			100%RH	50%RH	0%RH
30	Solvent Based	0% ¹	100%RH	50%RH	0%RH
	Nulam Blue Ink		53.88 ²	0.108 ²	0.023 ²
	Water Based	0%			
	Aqualam P White				
	Ink				
35	¹ Used 610-3M tape				
	² cc/100in ² /24hr				

The resulting film had high barrier properties having excellent printability.

EXAMPLE 2

5 An intimate blend of polypropylene (95 wt%) and maleated polypropylene (5 wt%) was prepared and formed into a cast layer of approximately 35 mls thick. This cast layer was then machine direction oriented to a thickness of about 1 ml thick. A coating of the above-identified poly(vinyl alcohol) was applied to one
10 surface each of a pair of the machine direction oriented polypropylene films. The poly(vinyl alcohol) coating contained 2.5 phr of ammonium chloride and 20 phr of Parex 613 maleine formaldehyde. The so-coated substrate films were mated together so that the
15 poly(vinyl alcohol) layers were in contact. This was accomplished by running the film through rollers at room temperature. The film traveled at approximately 50 fpm and was subjected to a pressure of 90 psi. Thereafter the film combination was heated to 160°C and
20 transverse direction oriented. The finished film had been machine direction oriented 7 times and transverse direction oriented 5 times.

The resulting laminated film strongly resisted delamination and was highly resistant to the
25 transmission of oxygen and water vapor during a 24 hr. period.

It is to be understood that instead of bringing together 2 separately formed coated machine direction oriented films a single poly(vinyl alcohol) coated film
30 can be folded on itself so that the poly(vinyl alcohol) faces are in contact and, after edge trimming, the film can be pressure laminated to itself, heated and transverse direction oriented before final windup for shipment to a converter.

It is to be understood that the outer surfaces of the completed lamination can have applied thereto any conventional coatings, such as, heat seal layers.

CLAIMS:

1. A film combination comprising :
 - a) an oriented polymeric substrate which either i) comprises an intimate blend of polypropylene with maleic acid anhydride modified polypropylene or ii) is otherwise susceptible of transmitting oxygen and water vapor and has a primer coating on at least one surface;
 - b) a layer of cross-linked polyvinyl alcohol on i) the intimate blend or ii) the primer coating;
 - c) a layer of a polymer comprising vinyl alcohol residues which may be as defined in b) or an intimate blend of a homo- or copolymer of vinyl alcohol, with an ethylene acrylic acid copolymer; and, optionally,
 - d) a layer as defined in a)i).
2. A film combination according to claim 1 wherein the intimate blend of a)i) comprises from 92.5 to 98.5% by weight of polypropylene and from 1.5 to 7.5% by weight maleic acid anhydride modified polypropylene.
3. A film combination according to claim 1 wherein a)ii) comprises a homopolymer or copolymer of polypropylene.
4. A film combination according to any preceding claim wherein the oriented polymeric substrate has been treated to a surface free energy of at least about 35 dynes/cm.

5. A film combination according to any preceding claim wherein the weight ratio of the intimate blend of (c) is from 2:1 to 1:2.
- 5 6. A film combination according to claim 5 wherein the intimate blend comprises polyvinyl alcohol and ethylene-acrylic acid copolymer.
7. A film combination according to any preceding claim having a metal layer deposited on the intimate blend of layer (c).
- 10 8. A film combination according to claim 7 wherein the metal comprises aluminum.
- 15 9. A film combination comprising a pair of films each comprising an oriented polymeric substrate comprising an intimate blend of polypropylene and a maleic acid anhydride modified polypropylene on which a coating of polyvinyl alcohol containing a cross-linking agent has been applied to a surface thereof while the pair of films have been
20 monoaxially oriented in the machine direction, the pair of films having been positioned with the polyvinyl alcohol layers in intimate contacting relationship while contacting films have been oriented in the transverse direction.
- 25 10. A film combination of claim 9 wherein the positioning is accompanied by a mating force of 30-130 psi.
11. A film combination according to any preceding claim which is oriented from 2 to 7 times MD and from 3 to 8 times TD.

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) :B29D 22/00; B32B 27/00

US CL :428/910, 520, 522, 36.6, 353

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 428/910, 520, 522, 36.6, 353

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US, A, 4,610,914 (NEWSOME) 09 SEPTEMBER 1986. See Abstract.	1-3, 9-10
A	US, A, 4,588,648 (KRUEGER ET AL) 13 MAY 1986. See Abstract.	1-3, 9-10

☐ Further documents are listed in the continuation of Box C.
 ☐ See patent family annex.

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be part of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E" earlier document published on or after the international filing date	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Z" document member of the same patent family
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

20 FEBRUARY 1993

Date of mailing of the international search report

04 MAY 1993

 Name and mailing address of the ISA/US
 Commissioner of Patents and Trademarks
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Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☒ Claims Nos.: 4, 5-8 and 11
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐

The additional search fees were accompanied by the applicant's protest.

☐

No protest accompanied the payment of additional search fees.